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NIST-Traceable-Reference-Material Optical Filters Program for Chemical Spectrophotometry

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Abstract

NIST has produced Standard Reference Materials for calibrating the wavelength scale and verifying the absorbance accuracy of UV/visible chemical spectrophotometers for several decades. The NIST production capacity is rapidly becoming insufficient to meet the demand, and a program developed recently to leverage NIST measurement capability through the private sector is being adapted to these standards. In general, NIST-Traceable Reference Materials (NTRMs) are commercially produced reference materials with well-defined traceability linkage to existing NIST Standards. Specifically, certifying laboratories will be accredited through the NIST-based National Voluntary Laboratory Accreditation Program (NVLAP) and will maintain periodic comparison measurements with the National Reference Spectrophotometer in the NIST Analytical Chemistry Division. The first NTRMs for chemical spectrophotometry will be modeled on NIST neutral density glass SRMs (in a cuvette-simulation format) certified at five

wavelengths in the visible spectral region and spanning absorbances between 0.3 and 2.0. The expanded uncertainties for the certified values will be kept close to those of the corresponding NIST standards by reducing the recertification period from two years to one, which will be compatible with the renewal cycle of many QC protocols and will provide more frequent cleaning of the filters. Other NTRMs will follow for wavelength calibration and UV absorbance verification.

Introduction

After 28 years of successful production and recertification of Standard Reference Materials® (SRMs) for the verification and calibration of UV/visible spectrophotometers (Figure 1), steadily increasing demand is putting the National Institute of Standards and Technology (NIST) optical filters program of the Analytical Chemistry Division (ACD) under intense pressure to re-define itself for the modern era. The demand for NIST optical filter SRMs now exceeds the ability of our small program to produce these labor-intensive standards, and commercial vendors are beginning to offer certified reference materials (CRMs) and calibration services traceable to NIST through their own NIST SRMs (Figure 2a). This is a healthy and necessary way to leverage the NIST measurement accuracy to the largest audience. However, the term "traceable to NIST" has been used so variably over the years that NIST is applying for a trademark registration for the term "NIST-Traceable Reference Material (NTRM™)" to designate a private sector CRM for which NIST has maintained an active participation in the entire certification process (Figure 2b).

The planning and design for the NTRM filters program has been based upon discussions and conclusions from three recent workshops attended by technically knowledgeable representatives from relevant industries. NTRM certifiers will satisfy requirements for accreditation by the National Voluntary Laboratory Accreditation Program (NVLAP) (1) and meet other specific requirements detailed in the NIST NTRM filters program documentation (2,3).

The International Vocabulary of Basic and General Terms in Metrology (VIM) defines traceability as: "Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties (4)." This article will not attempt to detail all of the elements of the NTRM protocol – which include annual accreditation with biennial, on-site audits, periodic direct and indirect proficiency testing, and continuous monitoring of all production and re-certification data and control charts. Instead, the following sections highlight the "links" in the traceability chain, using one member of the initial NTRM neutral density glass filter suite (a nominal 10 % transmitting filter) as an example to follow the propagation of uncertainties. Finally, we will speculate on the further evolution of the NTRM optical filters program.

The Reference Spectrophotometer

A new ACD reference spectrophotometer (Figure 3) is to be installed and commissioned in the new NIST Advanced Chemical Sciences Laboratory building in early 1999. This new national reference instrument includes features characteristic of high accuracy spectrophotometry (5) such as the use of the double aperture method for correcting the detection system non-linearity (6), a variable neutral density attenuator to adjust the reference reading to a fixed detector response for all measurement wavelengths, and an integrating-sphere-detection system to minimize the effects of beam distortion or deflection by the sample. Additional characteristic features include two stages of optical dispersion, and long optical paths in the monochromator and sample chamber to minimize stray radiant energy. Single beam geometry is used with bracketing background measurements averaged to correct for source drift to first order.

National reference spectrophotometers measure **regular transmittance**, *T*, which is defined as the fraction of a collimated beam incident normal to a sample that emerges without being absorbed or scattered. For solid reference materials such as the neutral density glass SRMs, NIST measures regular transmittance referred to air – that is, an empty filter holder is used in the beam for the background measurement. Thus, both reflective and absorptive losses are represented in the transmittance. The **transmittance density**, *TD*, values certified by NIST are computed from the measured regular transmittance in the same way as the **absorbance**, *A*, using the relationship $TD = A = -\log(T)$. NIST uses *TD* instead of *A* to indicate that a portion of the reported value arises from surface reflection in the case of transmittance density. For the current discussion, we ignore the semantic distinction and treat transmittance densities and their uncertainties in the more familiar "absorbance units" (AU), although absorbance and transmittance density are – in fact – unitless.

Table 1 shows representative uncertainty components for a 10 % transmitting NTRM filter. According to the NIST uncertainty policy (7), uncertainty components are expressed as either "Type A," evaluated by statistical means, or "Type B," evaluated by other means. In either case, uncertainty components, reported as "standard uncertainties," are constructed such that the standard uncertainty for a normally distributed population is equivalent to the estimated standard deviation. The uncertainties in the table are characterized according to their origin.

Uncertainty components attributed to the reference spectrophotometer are given in the first data column of Table 1. "Replication" represents the estimated standard deviation of a large number of independent readings, and an "instrumental" uncertainty component is included to account for possible errors in the corrections included for detector linearity, beam collimation and angle with respect to the normal to the filter, and inter-reflection effects. Near the bottom of the data column for the reference spectrophotometer, the combined uncertainty is computed as the root sum of squares of the uncertainty components in the column above. A factor of 2.0 is used to expand the uncertainty (in the bottom row), to correspond to a confidence interval of about 95 %. This uncertainty describes the accuracy of an absorbance measurement at a particular time, temperature, and geometric region on a sample. However, the ability to test spectrophotometers against each other depends as well upon material properties of the transfer standards.

NIST Standard Reference Materials

Table 2 gives a brief description of the various NIST optical properties SRMs shown in Figure 1. The materials are compatible with the most common sample holder in chemical spectrophotometry – the 10 mm pathlength cuvette – although some require the use of customer-supplied cuvettes. The solid absorbance standards are all mounted in aluminum frames constructed to the same dimensions as standard cuvettes (Figure 4).

The original and most widely disseminated NIST optical filter SRMs are based on neutral density glasses (8) and have been chosen as the initial filter type for the NTRM filters program. The glass is spectrally "neutral" in that the absorbance is nearly constant across the visible spectral range (Figure 5). Local minima and maxima still exist in spite of this overall neutrality, and certification is performed at five of these points of zero gradient to minimize any interactions between the absorbance and wavelength scales of the spectrophotometer being tested.

The second data column of Table 1 lists several uncertainties associated with neutral glass at a nominal absorbance of one (transmittance = 10 %) at all of the five certification wavelengths. The temperature component is based upon the small temperature coefficient of these glasses and a permissible usage range of 21 °C ± 2 °C for these filters. The heterogeneity component accommodates small changes in the absorbance of the glass over a 5 mm × 20 mm central region of the filter. The stability component allows for potential drift in the absorbance caused by changes in the surface reflectivity or surface contamination over the period of certification. The value of the stability component given in Table 1 for SRM filters is half of the normal value, since SRM filters used in the NTRM program will be re-certified annually instead of biennially.

At the bottom of the data column for the SRM, the combined uncertainty is computed using the root sum of squares of the uncertainty components in the column above <u>as well as those in the column for the reference spectrophotometer</u>. An expansion factor of 2.0 is again used to compute the expanded uncertainty in the bottom row, corresponding to a 95 % confidence interval for the final certified transmittance of the nominal 10 % transmitting SRM over a period of one year.

The Transfer Spectrophotometer

Each NTRM producer will identify one or more laboratory spectrophotometers to be designated as transfer spectrophotometers for the certification of NTRM filters. These instruments must be approved by NIST through a number of steps that constitute "qualification," and certain portions of this qualification procedure must be repeated periodically. Generic specifications characteristic of top-of-the-line commercial products set the minimum performance standards, and verification is required to ensure that these specifications are actually met. NIST SRMs and in-house working standards will be used to monitor the daily performance of the transfer spectrophotometers. NIST will have unlimited access to the data from control charts as well as routine measurements, to assess the long-term performance of the transfer spectrophotometers.

The third data column of Table 1 gives a set of fictitious, but plausible, uncertainty components for transfer spectrophotometers at an absorbance of unity (10 % transmittance). The replication uncertainty component is actually superior to that of the reference spectrophotometer, which sacrifices signal-to-noise ratio in favor of accuracy by employing an integrating-sphere-detection system. A Type B instrumental uncertainty component for the transfer spectrophotometer reflects the uncertainty of verification measurements against the reference spectrophotometer, with SRMs as the intermediate artifacts. This uncertainty component is taken to be equal to the combined uncertainty of the verifying SRM (given in the next-to-last row of the preceding column of Table 1). No further Type B uncertainties need be estimated for this instrument, since the accuracy is derived from the reference spectrophotometer through the artifact measurements.

The combined and expanded uncertainties below the third data column represent the accuracy of the transfer spectrophotometer alone. This instrumental uncertainty will necessarily be no less than the certified uncertainty of the artifacts used in the comparison measurements with the reference spectrophotometer, but is subject to improvement by reducing the time period between reference and transfer measurements (stability) and hand-selecting transfer artifacts for exceptional homogeneity (heterogeneity).

NIST-Traceable Neutral Glass Reference Materials

The NTRM optical filters to be produced first will meet or exceed the construction specifications of corresponding SRM filters and will be certified only at the nominal absorbances and wavelengths used for SRM filters. Certifiers may offer subsets of the NIST certification absorbances and wavelengths and may package filters in "sets" as they see fit. As the program matures, it may be valuable for NTRM producers to offer additional wavelengths and/or absorbances within the range spanned by the SRMs, to improve the coverage of NIST traceable measurements as well as their availability.

The Type B uncertainty components associated with nominally 10 % transmitting NTRM filters are listed in the fourth data column of Table 1 and are identical to those of SRMs, since the materials are constructed, heterogeneity-tested, and aged identically to SRMs. The stability component is again half of the value normally assigned to SRMs certified for a two-year period, since the NTRM filters will be certified for one year and the SRM filters used by the producers will also be recertified annually at NIST.

The combined uncertainty again includes the components in the column above as well as those in the column to the left, associated with the transfer spectrophotometer. The expanded uncertainty represents a "typical" value for a 95 % confidence interval at any of the five certification wavelengths for our fictitious example NTRM filter of absorbance one.

NTRMs and the End User

SRMs and NTRMs declare on their certificates that they are to be used to "verify the accuracy" of the transmittance and absorbance scales of molecular absorption spectrophotometers. The use of these materials for **verification** rather than **calibration** is a significant subtlety. It arises from the fact that molecular absorption spectrophotometry is based upon the self-normalizing ratio of the transmitted intensity to the incident intensity. The measurement is ultimately not traceable to any combination of the fundamental units of measurement. It is not even clear how one would use reference materials to "calibrate" an absorbance scale.

A common misunderstanding in the use of certified reference materials is the assumption that the certified uncertainties represent a "pass/fail" criterion for the field instrument whose accuracy is being verified. In fact, the uncertainty in the true value is relevant to the verification decision, but this only represents one side of the story. The instructions on the SRM 930e certificate suggest comparing the field instrument’s mean value and the user-defined tolerance with the certified value and the expanded uncertainty. "An acceptable level of agreement between a user’s measurements and the certified value is assured if any part of the range defined by the NIST certified value and its expanded uncertainty overlaps any part of the user’s tolerance band defined by the measured mean and the user-defined level of acceptable uncertainty (9)."

Figure 6 illustrates two entirely different uses of the range intersection test, designed to minimize either false negative results (6a) or false positive results (6b). Both parts of the figure represent an instrument reading at one (high absorbance) of the two pass/fail boundaries (extremes of the range intersection test) for the hypothetical reference material and the user-assigned "tolerance interval."

Figure 6a represents a case for which the user wishes to minimize false negative results, such as erroneously finding that the instrument is not within the factory-specified accuracy. The tolerance interval is taken as the accuracy desired. Since the expanded uncertainty for the reference material represents a two-sided 95 % confidence interval, there is at least a 97.5 % probability that the true value lies outside of the tolerance range (and the instrument is in need of repair) when the measured and certified values are separated by a greater amount than that shown.

In Figure 6b, a tolerance interval is defined which satisfies the need for a low probability of erroneously rating an instrument as acceptable for a test of a given required accuracy while still maintaining the simple range intersection criterion of the NIST certificate. The tolerance interval is defined so that the <u>entire</u> uncertainty range of the certified value must lie within the required accuracy of the measured mean for the instrument to "pass." Again, since the expanded uncertainty of the reference material assumes a two-tailed symmetric distribution, the probability of the true value falling within the desired range is $\geq$97.5 % as long as the measured and certified values are separated by the amount shown or less.

Taken together, the two examples of Figure 6 may be seen to illustrate the advisability of selecting an instrument whose factory specified accuracy exceeds the requirements of the application by at least two times the expanded uncertainty of the CRM used to verify the measurement accuracy. For such a choice, a low probability may be assured simultaneously for falsely failing a functioning instrument and falsely accepting an out-of-tolerance measurement.

What's Next?

The current goal is for NTRM optical filters to become available before the end of calendar year 1999. In the meantime, all the companies that intend to produce NTRM filters are selling CRM filters traceable to NIST through the use of SRM filters, using the "open loop" mode depicted in Figure 2a. Such filters that are produced with the necessary specifications may be convertible to NTRMs upon recertification, pending company policy and identification number issues.

The motivation for developing neutral glass NTRMs also applies to other NIST filter SRMs. In particular, the SRM 2031 series, which provides verification in the UV as well as the visible, is in great demand and may be a likely NTRM candidate. This solid filter suite is much more difficult to produce than the neutral glasses, involving accurate and homogeneous coating of chromium on fused silica substrates ground and polished to the same optical tolerances as the neutral glass and optically contacting a comparable cover plate onto the coated substrate. At least two commercial suppliers have recently been working to perfect the production of such filters.

The solid absorbance filter standards are individually certified using the reference spectrophotometer. The other spectrophotometric SRMs are batch certified, with measurements made on a statistical sampling of the entire production batch. Since such materials require fewer resources and represent a lesser production challenge for NIST than the individually certified standards, there is a correspondingly lower incentive to introduce them as NTRMs.

Finally, referencing practical measurements to fundamental constants and principles is preferable to the use of artifact transfer standards for the verification and calibration of spectrophotometers. For the absorbance axis, the decades-old double aperture method [6], which is not subject to contamination, surface chemistry, material inhomogeneity, or temperature dependence, is an attractive technique whose fundamental principles are straightforward. For the wavelength axis, atomic spectral lines in vacuum are quantum standards, are sufficiently tabulated in the open literature, and are much narrower and more symmetric than solid or liquid molecular absorption bands.

Although atomic line calibration and double aperture verification can be automated into processor-controlled instruments, artifact standards may be expected to play an important regulatory and quality assurance role for some time to come.

Acknowledgments

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Table 1
Representative Uncertainty Computation for NTRM Filters

Source[a]	Reference Spectrophotometer	SRM	Transfer Spectrophotometer[b]	NTRM
Replication (A)	0.00043	--	0.00030	--
Instrumental (B)	0.00030	--	0.0011	--
Temperature (B)	--	0.00050	--	0.00050
Heterogeneity (B)	--	0.00075	--	0.00075
Stability (B)	--	0.00038	--	0.00038
Combined	0.0005	0.0011	0.0011	0.0015
Expanded	0.0010	0.0022	0.0023	0.0030

[a] Parenthetical "(A)" denotes a Type A uncertainty component, and "(B)" a Type B uncertainty component.
[b] A fictitious number is used for "Replication," and the "Instrumental" component is taken as the combined uncertainty for the verifying SRM.

Table 2.
NIST Standard Reference Materials for UV/visible Spectrophotometry

SRM	Type	(Wavelength Range)/nm (No. of Wavelengths)	Unit Size
930e	Transmittance, neutral glass, T_{nom}= 0.1, 0.2, 0.3	440 to 635 (5)	3 filters+1 holder
931e	Absorbance, liquid, 3 levels & blank	302 to 678 (4)	Set of 12 ampoules
935a	Absorbance, potassium dichromate powder, 10 levels	235 to 350 (4)	15 g
1930	Transmittance, neutral glass, T_{nom}= 0.01, 0.03, 0.5	440 to 635 (5)	3 filters+1 holder
2030a	Transmittance, T_{nom}=0.3	465	1 filter+1 holder
2031a	Transmittance, metal-on-fused-silica, T_{nom}= 0.1, 0.3, 0.9	250 to 635 (10)	3 filters+1 holder
2032	Stray Light, potassium iodide	240 to 280 (9)	25 g
2034	Wavelength, Holmium Oxide Solution	240 to 650 (14)	1 sealed cuvette
2035	Wavelength, Rare Earth Glass, to be available in 1999	~1000 to 2000 (7)	2.5 cm disk in 5 cm holder

Figure Captions

Figure 1. Photograph of NIST spectrophotometric Standard Reference Materials (SRMs).

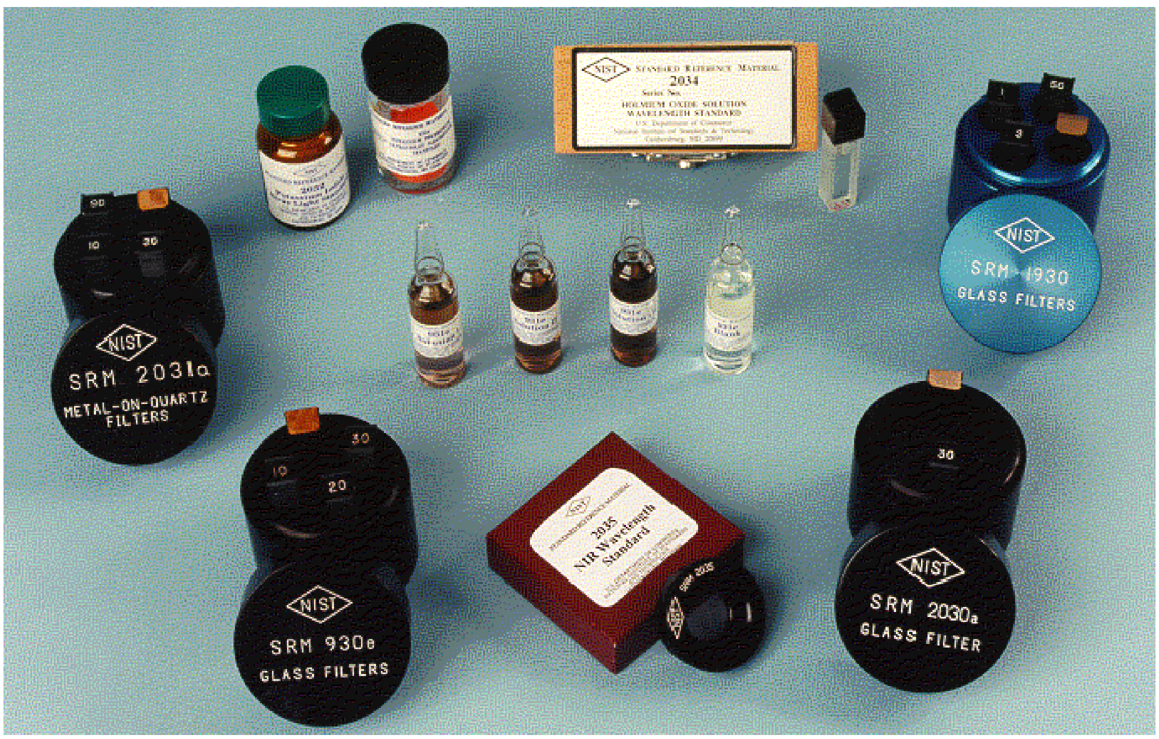
Figure 2. Concept diagram for (a) the "open-loop" certification of CRM optical filters "traceable to NIST" and (b) the "closed-loop" certification of NIST-traceable reference material (NTRM™) filters.

Figure 3. Diagram of the new NIST Analytical Chemistry Division reference spectrophotometer.

Figure 4. Assembly of solid absorbance filters into metal cuvette-simulation holders.

Figure 5. Representative spectra of the six nominal absorbance levels of neutral density glass SRM filters.

Figure 6. Representations of the use of the range intersection method (see text) – at one of two decision extremes – for (a) testing an instrument for adherence to factory specifications, and (b) testing the ability of an instrument to perform chemical measurements with a required accuracy.


STANDARD REFERENCE MATERIAL
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HOLMIUM OXIDE SOLUTION
WAVELENGTH STANDARD
SRM 2031a
METAL-ON-QUARTZ
FILTERS
SRM 1930
GLASS FILTERS
SRM 930e
GLASS FILTERS
2035
NIR Wavelength
Standard
SRM 2030a
GLASS FILTER

Figure 1

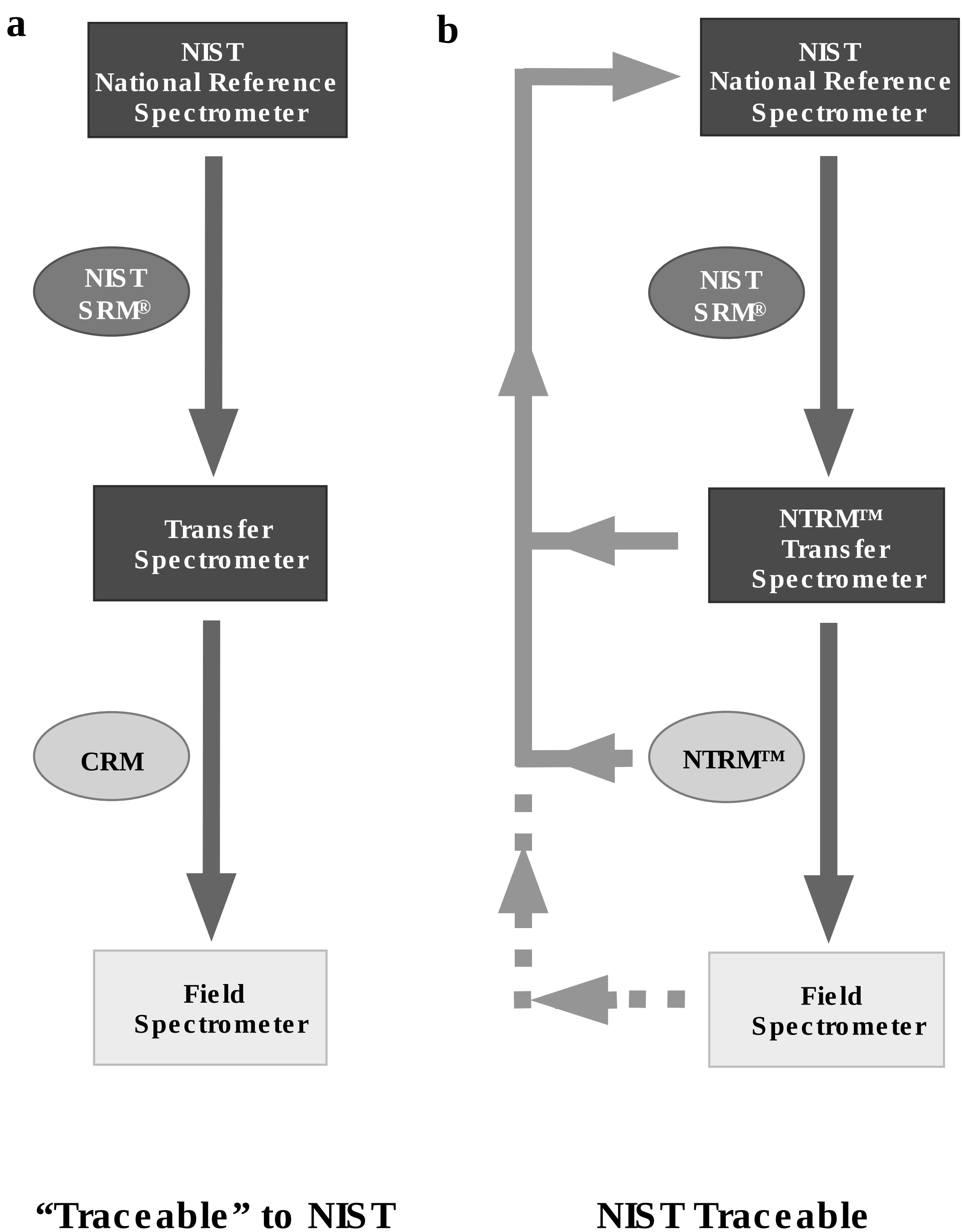

a
NIST
National Reference
Spectrometer
NIST
SRM®
Transfer
Spectrometer
CRM
Field
Spectrometer
b
NIST
National Reference
Spectrometer
NIST
SRM®
NTRM™
Transfer
Spectrometer
NTRM™
Field
Spectrometer
"Traceable" to NIST
NIST Traceable

Figure 2

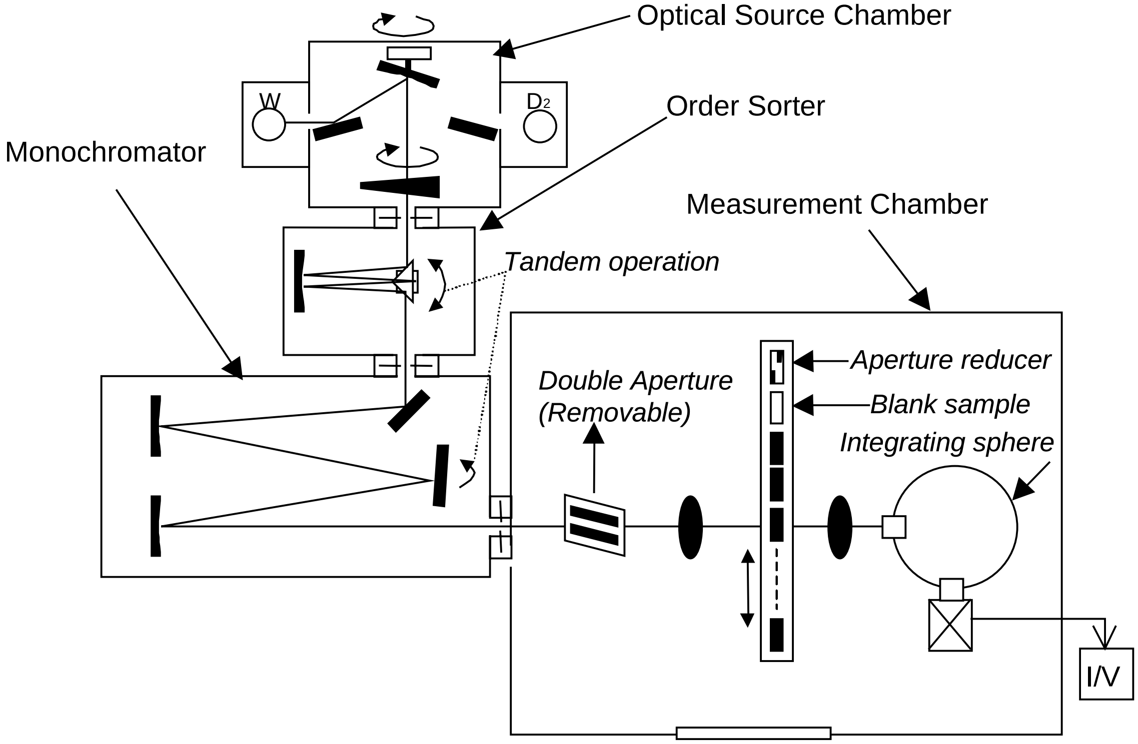

Optical Source Chamber
W
D2
Order Sorter
Monochromator
Measurement Chamber
Tandem operation
Aperture reducer
Double Aperture
(Removable)
Blank sample
Integrating sphere
I/V

Figure 3


National Institute of Standards & Technology
Certificate
Standard Reference Material® 930e
Glass Filters for Spectrophotometry
30-2207

Figure 4

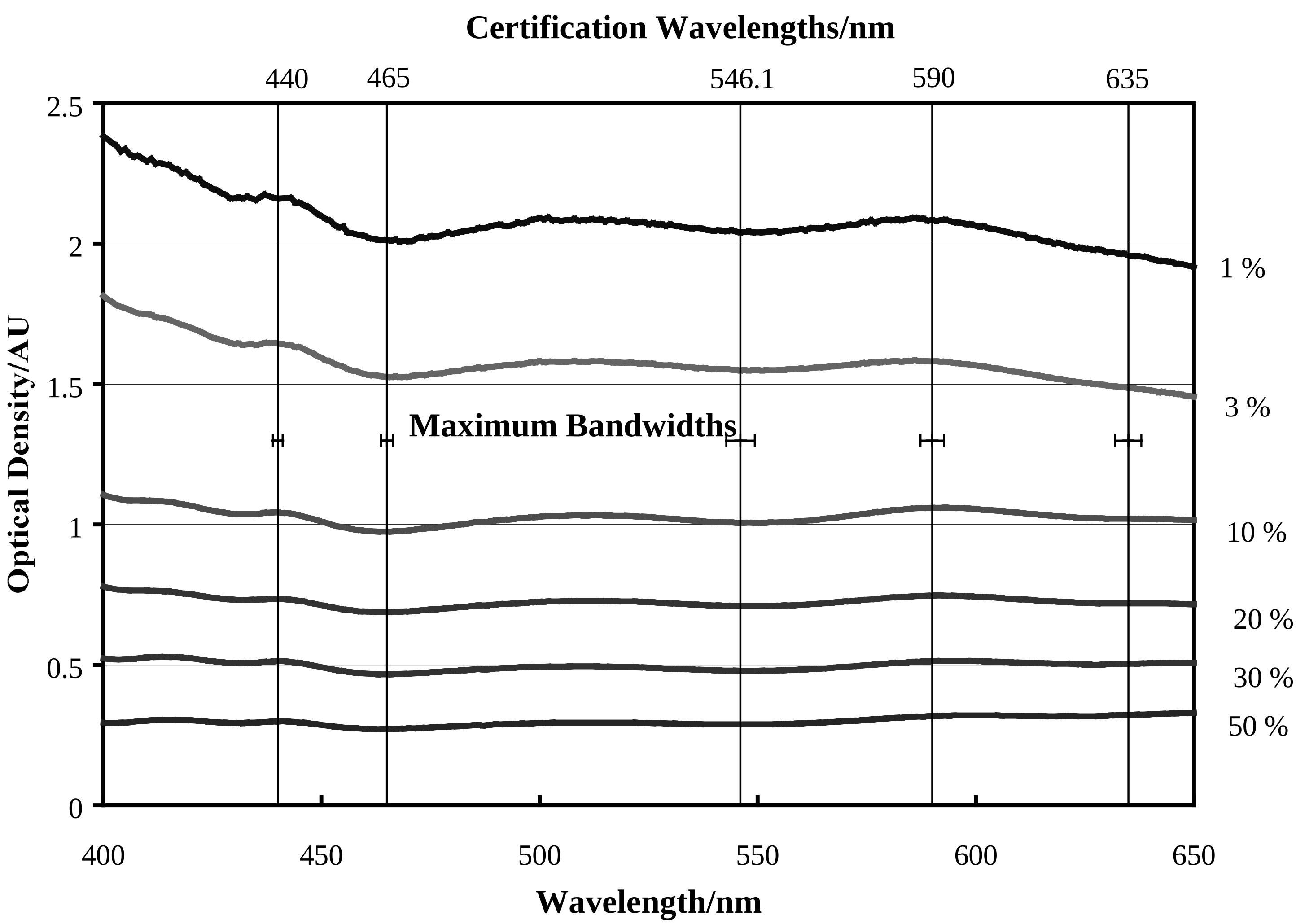
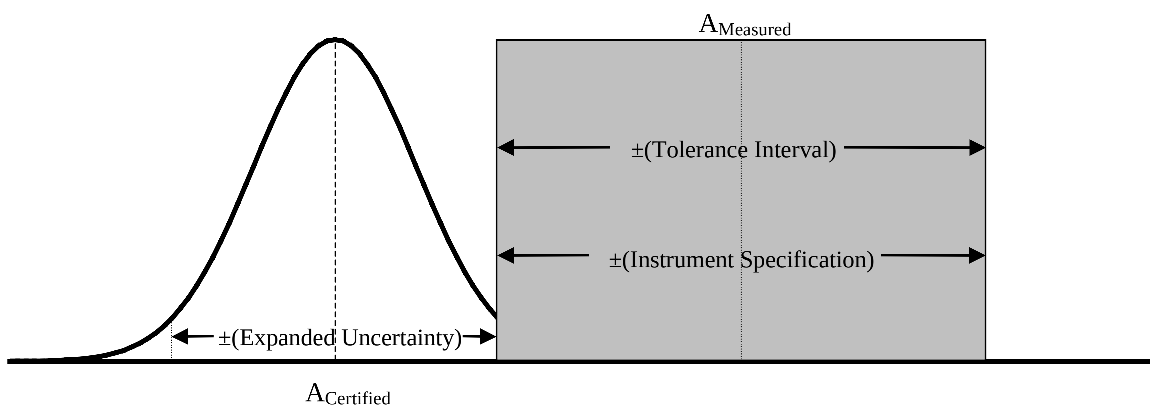

Certification Wavelengths/nm
440
465
546.1
590
635
Maximum Bandwidths
Optical Density/AU
2.5
2
1.5
1
0.5
0
400
450
500
550
600
650
Wavelength/nm
1 %
3 %
10 %
20 %
30 %
50 %

Figure 5

a


$A_{Measured}$
±(Tolerance Interval)
±(Instrument Specification)
±(Expanded Uncertainty)
$A_{Certified}$

b

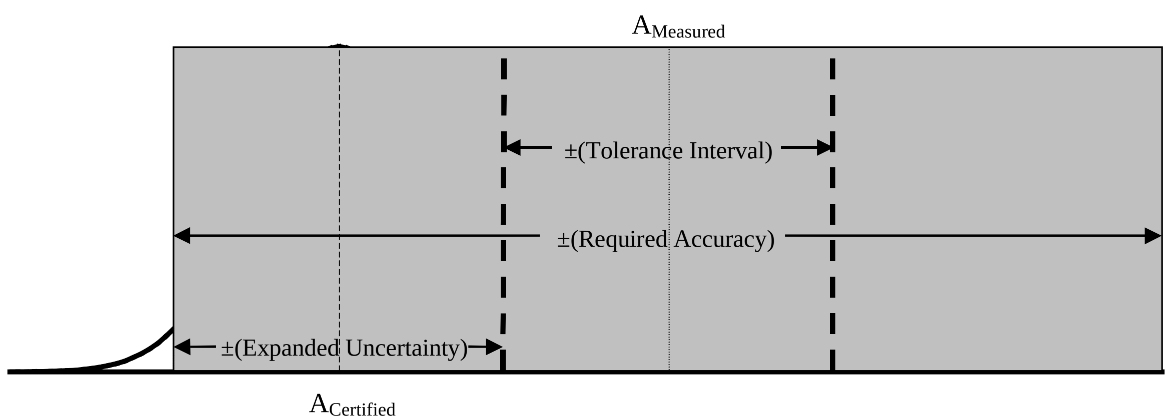

$A_{Measured}$
±(Tolerance Interval)
±(Required Accuracy)
±(Expanded Uncertainty)
$A_{Certified}$

Figure 6

References

1 James L. Cigler and Vanda R. White, editors, NVLAP Procedures and General Requirements, NIST Handbook 150, U.S. Government Printing Office, Washington, D.C. (1994).

2 G.W. Kramer, J.C. Travis, C.D. Faison, and S.D. Rasberry, Chemical Calibration: Certifiers of Spectrophotometric NTRMs, U.S. Government Printing Office, in preparation as NIST Handbook 150-zz, where the number "zz" is yet to be assigned, 1999.

3 J.C. Travis, M.V. Smith, S.D. Rasberry, and G.W. Kramer, Technical Specifications for Certification of Spectrophotometric NTRMs, U.S. Government Printing Office, Washington, D.C., in preparation as NIST Special Publication SP 260-zzz, with the number "zzz" to be assigned, 1999.

4 International Vocabulary of Basic and General Terms in Metrology, Second Edition, International Organization for Standardization, 1993.

5 R. Mavrodineanu, J. Res. Nat. Bur. Stand. (U.S.) **76A** (5), 405 – 425 (1972).

6 F.J.J. Clarke, J. Res. Nat. Bur. Stand. (U.S.) **76A** (5), 375 – 403 (1972).

7 B.N. Taylor and C.E. Kuyatt, editors, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, NIST Technical Note 1297, U.S. Government Printing Office, Washington, D.C., 1994.

8 R. Mavrodineanu, R. W. Burke, J.R. Baldwin, M.V. Smith, J.D. Messman, J.C. Travis, and J.C. Colbert, Glass Filters as a Standard Reference Material for Spectrophotometry – Selection, Preparation, Certification, and Use of SRM 930 and SRM 1930, NIST Special Publication 260-116, U.S. Government Printing Office, Washington, 1994.

9 Certificate, SRM 930e, Glass Filters for Spectrophotometry, Standard Reference Materials Program, NIST, Gaithersburg, MD, 12 May 1998.